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and the degree of conversion. Homopolymers, random copolymers or block polymers can be produced with a high degree of control and with low polydispersity. Swarc (*Adv. Polym. Sci.* 49, 1 (1983)) stated that living polymerization to give polymers of narrow molecular weight distribution requires the absence of chain transfer and termination reactions, the elementary reactions being only initiation and propagation, which take place uniformly with respect to all growing polymer chains. Later Inoue and Aida in an article on living polymer systems (*Encyclopedia of Polymer Science and Engineering*, Supplement Volume, Wiley Interscience New York 1989) stated "If chain transfer and terminating agents are present in the polymerization system the living character of the polymerization is lost, and the formation of polymer with narrow molecular weight distribution does not result."

However, it has been shown that if the chain transfer process is reversible then polymerization can still possess most of the characteristics of living polymerization. A variety of terms have been used to describe polymerizations believed to involve this mechanism including "immortal polymerization", "equilibration polymerization", "polymerization with degenerative chain transfer" and "living polymerization with reversible chain transfer". Quirk and Lee (*Polymer International* 27, 359 (1992)), who recommend the last terminology, point out that the Criteria 3 and 4 mentioned above need to be modified when describing these polymerizations to encompass the fact that the total number of polymer molecules is determined by the total number of moles of transfer agent plus the number of moles of initiator.

Block copolymer syntheses by free radical polymerization in the presence of certain dithiocarbamate or xanthate derivatives as initiator-transfer agents-chain terminators (iniferters) have been described. In these examples the dithiocarbamate or xanthate derivative is used as a photochemical initiator. For a discussion of this chemistry see recent reviews [Moad *et al.* in *Comprehensive Polymer Science*; Pergamon: London, vol 3, p 141 (1989)]. The dithiocarbamates (for example, benzyl dithiocarbamate) have very low transfer constants ( $\ll 0.1$ ) and are ineffective in the context of the current invention. Greszta *et al.* (*Macromolecules*, 27, 638 (1994)) have described the application of chain transfer chemistry in living radical polymerization and have proposed and rejected the use of dithiocarbamates in this context because of the low transfer constant and the problem of side reactions. JP 04198303 A2 discloses polymerization in the presence of triarylmethyl dithiocarboxylates of the following structure

controlling the polydispersity of the polymer being formed by varying the ratio of the number of molecules of (ii) to the number of molecules of (iii);

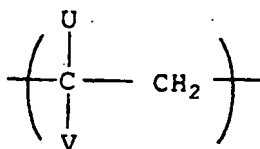
the polymer of Formula A being made by contacting (i), (ii)C and (iii) and the  
5 polymer of Formula B being made by contacting (i), (ii) D and (iii);

wherein:

10 Z is selected from the group consisting of hydrogen, chlorine, optionally substituted alkyl, optionally substituted aryl, optionally substituted heterocyclyl, optionally substituted alkylthio, optionally substituted alkoxycarbonyl, optionally substituted aryloxy carbonyl (-COOR"), carboxy (-COOH), optionally substituted acyloxy (-O<sub>2</sub>CR"), optionally substituted carbamoyl (-CONR"2), cyano (-CN), dialkyl- or diaryl- phosphonato [-P(=O)OR"2], dialkyl- or diaryl-phosphinato  
15 [-P(=O)R"2], and a polymer chain formed by any mechanism;

Z' is a m-valent moiety derived from a member of the group consisting of optionally substituted alkyl, optionally substituted aryl and a polymer chain; where the connecting moieties are selected from the group that consists of  
20 aliphatic carbon, aromatic carbon, and sulfur;

Q is selected from the group consisting of



and

25 repeating units from maleic anhydride, N-alkylmaleimide, N-arylmaleimide, dialkyl fumarate and cyclopolymerizable monomers;

U is selected from the group consisting of hydrogen, halogen, optionally substituted C<sub>1</sub>-C<sub>4</sub> alkyl wherein the substituents are independently selected from the group that consists of hydroxy, alkoxy, aryloxy (OR"), carboxy, acyloxy, aroyloxy (O<sub>2</sub>CR"), alkoxy- carbonyl and aryloxy-carbonyl (CO<sub>2</sub>R");  
30

V is selected from the group consisting of hydrogen, R", CO<sub>2</sub>H, CO<sub>2</sub>R", COR", CN, CONH<sub>2</sub>, CONHR", CONR"2, O<sub>2</sub>CR", OR" and halogen;

R is selected from the group consisting of optionally substituted alkyl; and  
optionally substituted saturated, unsaturated or aromatic carbocyclic or  
heterocyclic ring; optionally substituted alkylthio; optionally substituted alkoxy;  
optionally substituted dialkylamino; an organometallic species; and a polymer  
5 chain prepared by any polymerization mechanism; in compounds C and D, R• is a  
free-radical leaving group that initiates free radical polymerization;

R" is selected from the group consisting of optionally substituted C<sub>1</sub>-C<sub>18</sub>  
alkyl, C<sub>2</sub>-C<sub>18</sub> alkenyl, aryl, heterocyclyl, aralkyl, alkaryl wherein the substituents  
10 are independently selected from the group that consists of epoxy, hydroxy, alkoxy,  
acyl, acyloxy, carboxy (and salts), sulfonic acid (and salts), alkoxy- or aryloxy-  
carbonyl, isocyanato, cyano, silyl, halo, and dialkylamino;

15 q is 1 or an integer greater than 1;

p is 1 or an integer greater than 1; when  $p \geq 2$ , then  $R=R'$ ;

m is an integer  $\geq 2$ ; and

20 R' is a p-valent moiety derived from a member of the group consisting of  
optionally substituted alkyl, optionally substituted aryl and a polymer chain;  
where the connecting moieties are selected from the group consisting of aliphatic  
carbon, aromatic carbon, silicon, and sulfur; in compounds C and D, R• is a free  
radical leaving group that initiates free radical polymerization.

25 Preferred is a process as described for controlling polydispersity by  
varying the ratio of the number of molecules of (ii) to (iii) as follows:

- 30 (a) lower polydispersity by increasing the ratio of (ii) to (iii); and  
(b) increase polydispersity by decreasing the ratio of (ii) to (iii).

Most preferred is the process in which the ratio of (ii) to (iii) is increased to obtain  
a polymer having a polydispersity below about 1.5.

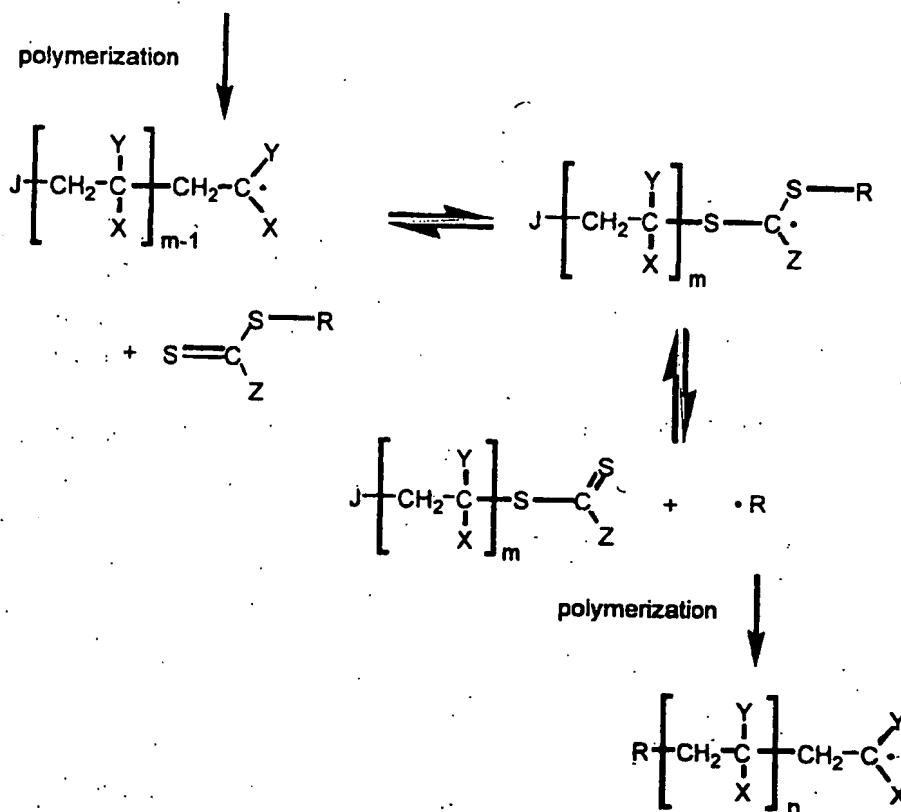
35 The monomer moieties and value of q in the monomer repeating unit(s)  
derived from those in (i) are selected so that:  
when  $q \geq 1$  and Q is a single monomer species, then the polymer is homopolymer;

Saturated, unsaturated, or aromatic carbocyclic or heterocyclic rings may contain from 3 to 14 atoms.

"Heterocyclic" or "heterocyclyl" means a ring structure containing 3 to 10 atoms at least one of which is selected from O, N and S, which may or may not be aromatic. Examples of aromatic "heterocyclyl" moieties are pyridyl, furanyl, thienyl, piperidinyl, pyrrolidinyl, pyrazoyl, benzthiazolyl, indolyl, benzofuranyl, benzothiophenyl, pyrazinyl, quinolyl, and the like, optionally substituted with one or more alkyl, haloalkyl, halo, nitro, or cyano groups. "Ph" means phenyl.

An example of the preferred class of CTAs are the dithioesters (Formula C, p=1) such as are depicted in Scheme 2 which is illustrative of the reaction mechanism believed to be operative in the process of this invention. It should be understood, however, that the invention is not limited to the mechanism depicted and that other mechanisms may be involved.

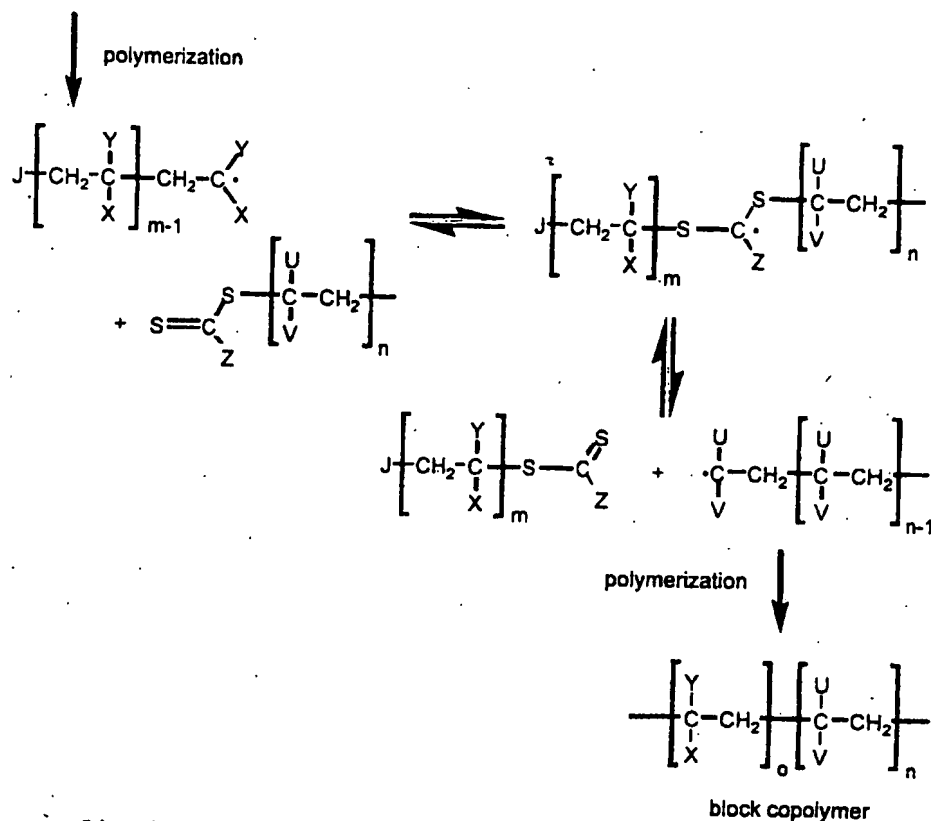
Scheme 2:



J is a fragment derived from an initiating or propagating radical.

A key feature of the invention is the retention of the active thiocarbonylthio end group  $[-C(S)-S-]$  in the polymeric product. The invention thus also provides a route to block polymers as illustrated, for example, in Scheme 3.

Scheme 3:



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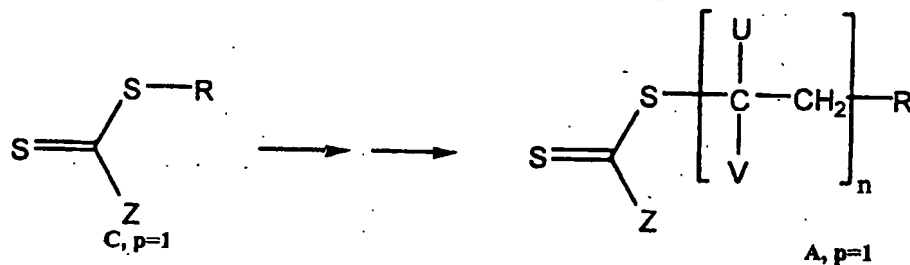
J is a fragment derived from an initiating or a propagating radical.

Polymers with complex architectures including multiblock, branched, star and graft polymers are available through the use of reagents containing multiple thiocarbonylthio groups as indicated by formulae C (where  $p \geq 2$ ) and D. The overall process is shown in Scheme 4.

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Scheme 4:

Formation of linear polymer from CTA of formula C,  $p=1$



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In the context of the present invention, low polydispersity polymers are those with polydispersities that are significantly less than those produced by conventional free radical polymerization. In conventional free radical polymerization, polydispersities (the  
5 polydispersity is defined as the ratio of the weight average and number average molecular weights -  $M_w/M_n$ ) of the polymers formed are typically in the range 1.6-2.0 for low conversions (<10%) and are substantially greater than this for higher conversions. Polydispersities obtained with the present invention are usually less than 1.5, often less than 1.3 and, with  
10 appropriate choice of the chain transfer agent and the reaction conditions, may be less than 1.1. The low polydispersity can be maintained at high conversions (see Examples).

Note that it is also possible to produce polymers with broad, yet controlled, polydispersity or multimodal molecular weight distribution by controlled addition of the CTA over the course of the polymerization  
15 process.

Müller et al. have derived relationships which enable polydispersities to be estimated for polymerizations which involve chain equilibration by reversible chain transfer (Müller, A.H.E.; Zhuang, R.; Yan, D.; Litvenko, G. *Macromolecules*, 1995, 28, 4326)  
20

$$M_w/M_n = 1 + 1/C_{tr}$$

This above relationship should apply to batch polymerizations carried to full conversion in the situation where the number of initiator-radical derived chains is small with respect to total chains and there are no side reactions.  
25

This relationship suggests that the transfer constant should be > 2 to obtain a polydispersity < 1.5 in a batch polymerization. If the transfer constant is < 2, low polydispersities (<1.5) may still be obtained in feed polymerization processes by choosing an appropriate monomer to transfer agent ratio and continuing the polymerization for a sufficient period to produce the desired molecular weight and polydispersity. In these  
30 circumstances, kinetic simulation can be used to aid in selecting reaction conditions.  
35

In theory, it is possible to use reagents with very low transfer constants (<0.1). However, in this case it is likely that side reactions will complicate the polymerization process. In practice, polydispersities are

likely to be higher than predicted by these relationships because of the limitations already mentioned. Nonetheless, these relationships serve as a useful guide in selecting reaction conditions.

5    b)    Molecular weights increase in a predictable and linear manner with conversion (see Examples) which is controlled by the stoichiometry. In the case of monofunctional CTAs of Formulae C and D the molecular weight of the product can be calculated according to the relationship:

$$10 \quad MW_{\text{prod}} = \frac{[\text{moles monomer consumed}]}{[\text{moles CTA}]} \times MW_{\text{mon}} + MW_{\text{cta}}$$

Where:  $MW_{prod}$  is the number average molecular weight of the isolated polymer

$MW_{\text{mon}}$  is the molecular weight of the monomer

MW<sub>cta</sub> is the molecular weight of the CTA of formula C or D.

This expression applies under reaction conditions where the number of initiator-derived chains is small with respect to total chains.

Note that this form of molecular weight control is very different to that seen in free radical polymerization in the presence of conventional transfer agents.

c) The process can be used to provide various low polydispersity polymers including:

- End-functional polymers
- Block and multiblock and gradient polymers
- Star polymers
- Graft or branched polymers.

d) The process of this invention is compatible with a wider range of monomers and reaction conditions than other processes for producing low polydispersity and reactive polymers. Specific advantages of the present process are:

i) The much higher transfer constant of compounds of Formula C or D (transfer constant can be  $>20$ ) in comparison to macromonomers (transfer constant  $<2$ ) means that it is not necessary to use starved-feed conditions to obtain low polydispersity polymers or block polymers. It is possible to use a batch polymerization process (see Examples).

- ii) The compounds of Formula C or D do not undergo copolymerization with *RL* monomers. Therefore, low polydispersity polymers based on monosubstituted monomers (e.g., acrylic monomers, styrene) can be carried out under a wider range of reaction conditions.

The choice of the CTA compound is important in synthesis of low polydispersity polymers. The preferred dithioesters and related compounds give chain transfer with high chain transfer constants.

The transfer constant is defined as the ratio of the rate constant for chain transfer to the rate constant for propagation at zero conversion of monomer and CTA compound. If chain transfer occurs by addition-fragmentation, the rate constant for chain transfer ( $k_{tr}$ ) is defined as follows:

$$k_{tr} = k_{add} \times \frac{k_{\beta}}{k_{-add} + k_{\beta}}$$

where  $k_{add}$  is the rate constant for addition to the CTA and  $k_{-add}$  and  $k_{\beta}$  are the rate constants for fragmentation in the reverse and forward directions respectively. Based on the addition-fragmentation mechanism, four factors can be seen to influence the effectiveness of the CTA in the process of this invention:

- The rate of reaction of the CTA ( $RA$  and  $AP_n$  in Scheme 1).
- The partitioning of the intermediate radicals ( $P_nA^*R$  and  $P_nA^*P_m$  in Scheme 1) between starting materials and products.
- The rate of fragmentation of the intermediate radicals ( $P_nA^*R$  and  $P_nA^*P_m$  in Scheme 1).
- The ability of the expelled radicals ( $R^*$  and  $P_n^*$  in Scheme 1) to reinitiate polymerization. Factors a) and b) determine the magnitude of the transfer constant of the CTA compound.

Preferably, the transfer constant for the addition-fragmentation chain transfer process is  $>0.1$ . The polydispersity obtained under a given set of reaction conditions is sensitive to the value of the transfer constant. Lower polydispersities will result from the use of reagents with higher transfer constants. Benzyl dithiobenzoate derivatives have transfer constants which are estimated to be  $>20$  in polymerization of styrene or acrylate esters. Higher transfer constants also allow greater flexibility in the choice of reaction conditions. For reagents with low chain transfer constants, the use of feed addition is advantageous to obtain low polydispersities.

The chain transfer activity of CTAs of Formula C or D is a function of the substituents  $R$  and  $Z$  and the particular propagating radical.  $R$  should be chosen



from 1,4 chloroform/ethanol gave the title compound as a red solid (77% yield), m.p. 222-224 °C (dec). <sup>1</sup>H-nmr (CDCl<sub>3</sub>) δ (ppm): 4.66 (s, 12H); 7.30-7.60 (m, 18H) and 7.94 (m, 12H).

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#### Example 4

**Preparation of 1,4-bis(thiobenzoylthiomethyl)benzene (8, Z=Ph) (C, p=2, R=C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>)<sub>2</sub>, Z = Ph)**

1,4-Bis(thiobenzoylthiomethyl)benzene was prepared from a,a'-dibromo-p-xylene according to the method described for the preparation of benzyl dithiobenzoate (3) with the modification that the reaction mixture was heated at 40°C for 1.5 hours. After the usual work-up, recrystallization from ethanol gave the title compound as a red solid (66.7% yield), m.p. 95-97°C. <sup>1</sup>H-nmr (CDCl<sub>3</sub>) δ (ppm): 4.60 (s, 4H); 7.34-7.60 (m, 6H) and 8.00 (m, 4H).

15

#### Example 5

**Preparation of 1,2,4,5-tetrakis(thiobenzoylthiomethyl)benzene (9) (C, p=4, R=C<sub>6</sub>H<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>, Z = Ph)**


1,2,4,5-Tetrakis(thiobenzoylthiomethyl)benzene was prepared from 1,2,4,5-tetrakis-(bromomethyl)benzene according to the method described for the preparation of benzyl dithiobenzoate (3) with the modification that the reaction mixture was heated at 40 °C for 1 hour. The usual work-up gave a red solid which was recrystallized from 1:4 benzene/ethanol to give 1,2,4,5-tetrakis(thiobenzoylthiomethyl)benzene (47% yield), m.p. 142-143.5 °C (dec). <sup>1</sup>H-nmr (CDCl<sub>3</sub>) δ (ppm): 4.65 (s, 8H); 7.30-7.58 (m, 14H) and 7.97 (m, 8H).

25

#### Example 6

**Preparation of 1,4-bis-(2-(thiobenzoylthio)prop-2-yl)benzene (10) (C, p=2, R=1,4-C<sub>6</sub>H<sub>4</sub>(C(CH<sub>3</sub>)<sub>2</sub>)<sub>2</sub>, Z = Ph)**

1,4-diisopropenylbenzene (3.96 g) was added to a solution of dithiobenzoic acid (8 g) in carbon tetrachloride (50 mL) and the mixture heated at 70 °C for 16 hours. Removal of the solvent, followed by trituration with 1:2 diethyl ether/n-hexane allowed isolation of the title compound as a purple solid (2.87 g, 24.6% yield), m.p. 143-145 °C (dec). <sup>1</sup>H-nmr (CDCl<sub>3</sub>) δ (ppm): 2.00 (s, 12H); 7.33 (m, 4H); 7.49 (m, 2H); 7.50 (s, 4H) and 7.86 (m, 4H).

g, 24.3 % yield).  $^1\text{H}$ -nmr ( $\text{CDCl}_3$ )  $\delta$ (ppm): 1.25 (t, 3H); 2.90 (s, 3H); 4.07 (s, 2H) and 4.20 (q, 2H). 

#### Example 8

5 **Preparation of 2-(ethoxycarbonyl)prop-2-yl dithiobenzoate (14)** (C, p=1, R =  $\text{C}(\text{CH}_3)_2\text{COOEt}$ ; Z = Ph)

Phenyl magnesium bromide was prepared from bromobenzene (6.28 g, 0.04 mol) and magnesium turnings (1 g) in dry THF (30 mL). The solution was warmed to 40°C and carbon disulfide (3.05 g, 0.04 mol) was added over 15  
10 minutes while maintaining the reaction temperature at 40°C. To the resultant dark brown solution was added ethyl  $\alpha$ -bromoisobutyrate (7 g, 0.036 mol). The reaction temperature was raised to 80°C and maintained for 60 hours. Ice water (50 mL) was added and the organic products were extracted with diethyl ether (3 X 50 mL). The combined organic extracts were washed with water, brine and  
15 dried over anhydrous magnesium sulfate. After removal of solvent and purification by column chromatography (Kieselgel-60, 70-230 mesh, *n*-hexane/diethyl ether (9:1) eluent), 2-(ethoxycarbonyl)prop-2-yl dithiobenzoate was obtained as a red oil (4.52 g, 42.2% yield).  $^1\text{H}$ -nmr ( $\text{CDCl}_3$ )  $\delta$  (ppm): 1.25 (t, 3H,  $\text{CH}_2\text{CH}_3$ ), 1.77 (s, 6H,  $2\times\text{CH}_3$ ), 4.17 (q, 2H,  $\text{OCH}_2\text{CH}_3$ ), 7.35 (dd, 2H, meta-ArH), 7.52 (dd, 1H, para-ArH) and 7.95 (d, 2H, ortho-ArH).  
20

#### Example 9

**Preparation of 2-cyanoprop-2-yl dithiobenzoate (15)** (C, p=1, R =  $\text{C}(\text{CH}_3)_2\text{CN}$ ; Z = Ph)

25 2-Bromo-2-cyanopropane was prepared by the procedure of Chrzaszczewska and Popiel (*Roczniki Chem.*, 7, 74-8 (1927); *Chem. Abstr.*, (1928) 22:1343<sup>6</sup>). 2-Cyanoprop-2-yl dithiobenzoate (15) was prepared from 2-bromo-2-cyanopropane by a method similar to that used to prepare compound (14) with the modification that the reaction was maintained at 50°C for 24 hours.  
30 After work-up and purification (column chromatography on Kieselgel-60, 70-230 mesh, *n*-hexane/diethyl ether 9:1 eluent), 2-cyanoprop-2-yl dithiobenzoate (15) was obtained as a dark red oil (1.9 g, 43% yield).  $^1\text{H}$ -nmr ( $\text{CDCl}_3$ )  $\delta$  (ppm): 1.95 (s, 6H,  $2\times\text{CH}_3$ ), 7.38 (dd, 2H, meta-ArH), 7.57 (dd, 1H, para-ArH) and 7.92 (d, 2H, ortho-ArH).  $^{13}\text{C}$ -nmr ( $\text{CDCl}_3$ )  $\delta$  (ppm): 26.5, 41.7, 120.0 (CN), 126.6,  
35 128.5, 132.9, 144.5 and 227.

#### Procedure 6

**Preparation of *tert*-butyl dithiobenzoate (16)** (C, p=1, R =  $\text{C}(\text{CH}_3)_3$ ; Z = Ph)

The synthesis of *t*-butyl dithiobenzoate (16) was carried out in two steps.

i) S-*t*-butyl thiobenzoate *t*-Butyl mercaptan (6.15 g, 0.068 mol) was added dropwise to a solution of benzoyl chloride (10.5 g, 0.075 mol) in pyridine (6 g). The resulting mixture was allowed to stir for two hours at room temperature then poured onto ice-water and the mixture extracted with diethyl ether. The organic extract was washed with dilute HCl, water and brine and finally dried over anhydrous sodium sulfate. After removal of solvent and vacuum distillation, S-*t*-butyl thiobenzoate was obtained (6.64 g, 50.1% yield), b.p. 86°C (0.8 mmHg). <sup>1</sup>H-nmr (CDCl<sub>3</sub>) δ (ppm): 1.60 (s, 9H, 3xCH<sub>3</sub>), 7.41 (m, 2H, ArH), 7.54 (m, 1H, ArH) and 7.94 (d, 2H, ArH). <sup>13</sup>C-nmr (CDCl<sub>3</sub>) δ (ppm): 29.8, 48.0, 126.8, 128.3, 132.7, 138.6 and 192.9.

ii) *t*-Butyl Dithiobenzoate

A mixture of S-*t*-butyl thiobenzoate (1.94 g, 0.01 mol) and Lawesson's reagent (2.43 g, 0.006 mol) in anhydrous toluene (10 mL) was refluxed for 25 hours. After cooling to room temperature, the reaction mixture was concentrated and the residue subjected to column chromatography (Kieselgel-60, 70-230 mesh, petroleum spirit/diethyl ether 19:1) The title compound was obtained as an oil, 1.37g (65.5%). <sup>1</sup>H-nmr (CDCl<sub>3</sub>) δ (ppm): 1.69 (s, 9H, 3xCH<sub>3</sub>), 7.36 (m, 2H, meta-ArH), 7.50 (m, 1H, para-ArH) and 7.88 (d, 2H, ortho-ArH). <sup>13</sup>C-nmr (CDCl<sub>3</sub>) δ (ppm): 28.2, 52.2, 126.6, 128.1, 131.7 and 147.0. The signal due to C=S (δ > 220.0 ppm) was beyond the frequency range of the spectrum.

Example 10

**Preparation of 2,4,4-trimethylpent-2-yl dithiobenzoate (17) (C, p=1, R = C(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub>; Z = Ph)**

A mixture of dithiobenzoic acid (5 g), 2,4,4-trimethylpentene (7.3 g) and carbon tetrachloride (25 mL) was heated at 70 °C for two days. The resultant mixture was reduced to a crude oil. Purification of the residue, by column chromatography (Kieselgel-60, 70-230 mesh, petroleum spirit 40-60°C eluent) gave 2,4,4-trimethylpent-2-yl dithiobenzoate (17) (2.74 g, 31.7% yield) as a dark red oil. <sup>1</sup>H-nmr (CDCl<sub>3</sub>) δ (ppm): 1.08 (s, 9H, 3xCH<sub>3</sub>), 1.77 (s, 6H, 2xCH<sub>3</sub>), 2.20 (s, 2H, CH<sub>2</sub>), 7.35 (dd, 2H, meta-ArH), 7.49 (dd, 1H, para-ArH) and 7.85 (d, 2H, ortho-ArH). <sup>13</sup>C-nmr (CDCl<sub>3</sub>) δ (ppm): 28.3, 31.5, 32.8, 50.5, 57.7, 126.6, 128.1, 131.5 and 147.9. The signal due to C=S (δ > 220.0 ppm) was beyond the frequency range of the spectrum.

(Kieselgel-60, 70-230 mesh, 1:4 ethyl acetate/*n*-hexane eluent), ~~S~~benzyl diethoxyphosphinyldithioformate (20) was obtained (11 g, 18% yield) as a red oil. <sup>1</sup>H-nmr (CDCl<sub>3</sub>) δ (ppm) 1.43 (t, 6H); 4.38 (s, 2H), 4.65 (q, 4H) and 7.30-7.45 (m, 5H). *ML*

5

#### Procedure 8

**Preparation of *tert*-butyl trithioperbenzoate (21)** (C, p=1; R = (CH<sub>3</sub>)<sub>3</sub>CS; Z = Ph)

The title compound (21) was prepared according to the procedure described by Aycock and Jurch, *J. Org. Chem.*, **44**, 569-572, (1979). The residue was subjected to column chromatography (Kieselgel-60, 70-230 mesh, *n*-hexane eluent) to give the product, *tert*-butyl trithioperbenzoate (21) as a dark purple oil in 60 % yield. <sup>1</sup>H-nmr (CDCl<sub>3</sub>) δ (ppm) 1.32 (s, 9H), 7.45 (m, 3H) and 8.00 (m, 2H).

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#### Example 13

**Preparation of 2-phenylprop-2-yl 4-chlorodithiobenzoate (22)** (C, p=1, R = C(CH<sub>3</sub>)<sub>2</sub>Ph; Z = *p*-ClC<sub>6</sub>H<sub>4</sub>)

A mixture of 4-chlorodithiobenzoic acid (13 g) and *a*-methylstyrene (15 mL) were heated at 70°C for 1 hour. To the reaction mixture was added *n*-hexane (30 mL) and heating was continued at 70°C for 16 hours. The resultant mixture was reduced to a crude oil. Purification, of the oil by chromatography (aluminium oxide column (activity II-III) *n*-hexane eluent) gave the title compound (22) as a purple oil (8.5 g, 40 %). <sup>1</sup>H-nmr (CDCl<sub>3</sub>) δ (ppm) 2.00 (s, 6H); 7.30 (m, 5H); 7.55 (d, 2H) and 7.83 (d, 2H).

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#### Example 14

**Preparation of 2-phenylprop-2-yl 1-dithionaphthalate (23)** (C, p=1, R = C(CH<sub>3</sub>)<sub>2</sub>Ph; Z = 1-naphthyl)

The procedure was analogous to that used for the preparation of compound (5). The reaction of 1-(chloromethyl)naphthalene (17.6 g, 0.1 mol), sulfur (6.4 g, 0.2 mol) and sodium methoxide (25% solution in methanol, 46 mL) in methanol (50 mL) gave 1-dithionaphthoic acid (10 g, 49%). A mixture of 1-dithionaphthoic acid (10 g) and *a*-methylstyrene (10 mL) in carbon tetrachloride (20 mL) was heated at 70 °C for 16 hours. After removal of carbon tetrachloride and unreacted *a*-methylstyrene, the residue was chromatographed (Kieselgel-60, 70-230 mesh, 5% diethyl ether in *n*-hexane eluent) to yield 2-phenylprop-2-yl 1-dithionaphthalate (23) (9.2 g, 58 %) as a dark red oil. <sup>1</sup>H-nmr (CDCl<sub>3</sub>) δ (ppm) 2.06 (s, 6H); 7.29-7.55 (m, 7H); 7.66 (m, 2H); 7.85 (m, 2H) and 8.00 (m, 1H).

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**Table 4: Molecular weight and conversion data for polystyrene prepared with 2-phenylprop-2-yl dithiobenzoate at 60°C**

Entry	time/hr	M <sub>n</sub>	M <sub>w</sub> /M <sub>n</sub>	% Conv.
1 (control)	1	285 000	1.63	1.67
2	1	833	1.12	0.49
3	4	4 510	1.09	3.74
4	20	21 500	1.14	19.45
5	50	40 000	1.17	37.49
6	100	52 000	1.18	57.33

#### Example 25

- 5 **Preparation of low polydispersity polystyrene via thermal polymerization of styrene using 1-phenylethyl dithiobenzoate (4) at 100°C**

A stock solution of styrene (10 mL) and 1-phenylethyl dithiobenzoate (4) (24.8 mg) was prepared. Aliquots (2 mL) of this solution were transferred to ampoules which were degassed, sealed and heated at 100 °C for the times

- 10 indicated in Table 5 below and analyzed by GPC.

**Table 5: Molecular weight and conversion data for polystyrene prepared with 1-phenylethyl dithiobenzoate (4) at 100°C**

Entry	time/hr	M <sub>n</sub>	M <sub>w</sub>	M <sub>w</sub> /M <sub>n</sub>	% Conv.
1 (Control)	6	227 000	434 000	1.91	21.7
2	6	5 800	6 300	1.09	9.7
3	20	22 000	25 000	1.15	36.8
4	64	38 500	47 000	1.22	70.6
5	120	50 000	61 000	1.23	91.9

#### Example 26

- 15 **Preparation of low polydispersity polystyrene via thermal polymerization of styrene using 1-phenylethyl dithiobenzoate (4) at 100°C**

Example 25 was repeated with a threefold higher concentration of 1-phenylethyl dithiobenzoate (4) (75.6 mg) in the stock solution. The results are summarized in the Table 6 below.

✓  
The experimental conditions described in Example 19 (same molar concentrations) were used to prepare low polydispersity poly(methyl methacrylate) with *tert*-butyl trithioperbenzoate (21). After heating at 60 °C for 16 hours, poly(methyl methacrylate) was obtained (62.8% conversion; Mn 92 000; Mw/Mn 1.34).

#### Example 48

##### **Preparation of low polydispersity poly(methyl methacrylate) with 2-phenylprop-2-yl 4-chlorodithiobenzoate (22)**

The experimental conditions described in Example 19 (same molar concentrations) were used to prepare low polydispersity poly(methyl methacrylate) with 2-phenylprop-2-yl 4-chlorodithiobenzoate (22). After heating at 60 °C for 16 hours, poly(methyl methacrylate) was obtained (95 % conversion; Mn 55 000; Mw/Mn 1.07).

#### Example 49

##### **Preparation of low polydispersity poly(methyl methacrylate) with 2-phenylprop-2-yl 1-dithionaphthalate (23)**

The experimental conditions described in Example 19 (same molar concentrations) were used to prepare low polydispersity poly(methyl methacrylate) with 2-phenylprop-2-yl 1-dithionaphthalate (23). After heating at 60 °C for 16 hours, poly(methyl methacrylate) was obtained (95 % conversion; Mn 57500; Mw/Mn 1.10).

#### Example 50

##### **Preparation of low polydispersity poly(methyl methacrylate) in presence of 2-phenylprop-2-yl dithiobenzoate (5) with benzoyl peroxide as initiator**

A stock solution containing methyl methacrylate (20 mL), benzoyl peroxide (24.2 mg) and benzene (5 mL) was prepared. An aliquot (5 mL) of the stock solution was removed and 4mL of this was placed in an ampoule labelled as control run (entry 1). 2-phenylprop-2-yl dithiobenzoate (5) (54.5 mg) was added to the remaining 20 mL of stock solution. Aliquots of this solution (4 mL) were transferred to four ampoules which were degassed, sealed and heated at 60 °C. The results are summarized in Table 20 below.

Table 20: Molecular weight and conversion data for poly(methyl methacrylate) prepared with 2-phenylprop-2-yl dithiobenzoate (5) at 60 °C.

Entry	time/hr	$M_n$	$M_w/M_n$	% Conv.
1 (control)	2	453 000	1.81	11.1
2	2	6 080	1.40	6.8
3	4	10 300	1.28	14.8
4	8	20 000	1.17	33.4
5	16	41 000	1.13	77.9

- 5 The following example shows that polymerizations can be successfully carried out in both polar and nonpolar solvents.

Example 51

Preparation of low molecular weight and low polydispersity poly(methyl methacrylate) using 2-phenylprop-2-yl dithiobenzoate (5) in solvents such as benzene or 2-butanone (MEK).

Stock solutions were prepared by adding methyl methacrylate (15 mL) and azobisisobutyronitrile (100 mg) to the required solvent (5 mL). Aliquots (10 mL) of each stock solution and appropriate amount of 2-phenylprop-2-yl dithiobenzoate (5) (see Table 23) were transferred to ampoules which were degassed and heated at 60°C for specified times. Results are summarized in Table 21 below.

Table 21: Molecular weight and conversion data for poly(methyl methacrylate) prepared with 2-phenylprop-2-yl dithiobenzoate (5) at 60 °C in various solvents

Dithioester (g)	Time (hr)	Solvent	$M_n$	$M_w/M_n$	% Conv.
1.00	63.58	Benzene	3 200	1.17	79.8
0.40	24	Benzene	6 600	1.21	95.0
1.00	63.58	2-butanone	2 800	1.17	61.3
0.40	24	2-butanone	6 300	1.19	90.2

Example 52

Solution polymerization of methyl methacrylate (25%) with 2-phenylprop-2-yl dithiobenzoate (5)

A series of methyl methacrylate polymerizations were carried out with 2-phenylprop-2-yl dithiobenzoate (5). The results (see Table 24) when compared

with control experiments clearly indicate that in the presence of dithioester there is some retardation (conversions are ca. 10% less for the same reaction time). *ml*

A stock solution containing methyl methacrylate (10 mL), benzene (30 mL) and azobisisobutyronitrile (40 mg) was prepared. The stock solution was divided into two 20mL portions. The first 20mL portion was used for the 'control' experiments (entries 1-4). 2-phenylprop-2-yl dithiobenzoate (5) (100 mg) was added to the second 20mL portion (entries 5-8). Aliquots (4 mL) of these solutions were transferred to ampoules which were degassed, sealed and heated at 60 °C for the specified period of time.

Results are summarized in Table 22 below.

**Table 22: Molecular weight and conversion data for poly(methyl methacrylate) prepared with 2-phenylprop-2-yl dithiobenzoate (5) at 60 °C in benzene**

Entry	time/hr	parameter	control (no CTA)	with CTA (5)
1	2	$M_n$	98400	2880
		$M_w/M_n$	1.83	1.31
		% Conv.	20.3	10.7
2	4	$M_n$	88500	4570
		$M_w/M_n$	1.84	1.24
		% Conv.	35.3	23.5
3	16	$M_n$	69800	9250
		$M_w/M_n$	1.86	1.29
		% Conv.	82.3	71.6
4	30	$M_n$	58400	11720
		$M_w/M_n$	1.91	1.25
		% Conv.	95.0	88.7

15

### Example 53

**Preparation of low polydispersity polystyrene via bulk polymerization of styrene using 2-(ethoxycarbonyl)prop-2-yl dithiobenzoate (14)**

A stock solution of azobisisobutyronitrile (14.08 mg) in styrene (50 mL) was prepared. Aliquots (5 mL) of the stock solution were transferred to ampoules containing 2-(ethoxycarbonyl)prop-2-yl dithiobenzoate (14) (11.26 mg) which were degassed and sealed under vacuum. The ampoules were heated at 60°C for periods of time indicated in Table 23 below.

20



Table 23: Molecular weight and conversion data for polystyrene prepared with 2-(ethoxycarbonyl)prop-2-yl dithiobenzoate (14) at 60 °C

Entry	time/hr	M <sub>n</sub>	M <sub>w</sub> /M <sub>n</sub>	% Conv.
1	2	1 630	1.13	1.90
2	4	3 500	1.12	4.02
3	20	24 200	1.15	26.35

#### Example 54

- 5 Preparation of low polydispersity polystyrene via bulk polymerization of styrene using 2,4,4-trimethylpent-2-yl dithiobenzoate (17)

Example 53 was repeated with the exception that the dithioester used was 2,4,4-trimethylpent-2-yl dithiobenzoate (17) (same molar concentrations). The results are summarized in Table 24 below.

- 10 Table 24: Molecular weight and conversion data for polystyrene prepared with 2,4,4-trimethylpent-2-yl dithiobenzoate (17) at 60 °C

Entry	time/hr	M <sub>n</sub>	M <sub>w</sub> /M <sub>n</sub>	% Conv.
1	2	495	1.13	0.57
2	4	1 180	1.14	1.28
3	20	17 400	1.19	18.55

#### Example 55

- 15 Preparation of low polydispersity polystyrene via thermal polymerization of styrene with S-benzyl diethoxyphosphinyldithioformate (20)

A stock solution of styrene (10 mL) and S-benzyl diethoxyphosphinyldithioformate (20) (30.9 mg) was prepared. Aliquots (2 mL) of the stock solution were transferred to ampoules which were degassed and sealed. The first three ampoules (Table 25, entries 1-3), were heated at 100 °C and the final ampoule (Table 25, entry 4), was heated at 120 °C. Samples were removed at the time intervals indicated in the Table below and analyzed by GPC. The molecular weight increased linearly with % conversion and narrow polydispersities are maintained throughout the polymerization.

**Table 25: Molecular weight and conversion data for polystyrene prepared with benzyldiethoxyphosphinyldithioformate (20) at 100 °C**

Entry	Time/hr	M <sub>n</sub>	M <sub>w</sub> /M <sub>n</sub>	% Conv.
1 <sup>a</sup>	6	15 900	1.11	12.1
2 <sup>a</sup>	20	46 100	1.13	38.0
3 <sup>a</sup>	64	79 300	1.25	77.8
4 <sup>b</sup>	22	73 500	1.37	88.9

(a) Entries 1-3: The polymerizations were conducted at 100°C.

(b) Entry 4: The polymerization was conducted at 120°C.

5

#### Example 56

**Preparation of low polydispersity polystyrene via thermal polymerization of styrene at 110 °C with 2-phenylprop-2-yl dithiobenzoate (5)**

Example 27 was repeated with the exception that the reaction temperature used was 110 °C instead of 100 °C. After 16 hours at 110 °C, polystyrene (55% conversion) with M<sub>n</sub> 14 400 and M<sub>w</sub>/M<sub>n</sub> 1.04 was obtained.

10

The following two Examples demonstrate the use of the invention to prepare polymers with functional end groups (e.g. carboxylic acid).

15

#### Example 57

**Preparation of low polydispersity polystyrene via thermal polymerization of styrene with carboxymethyl dithiobenzoate (27)**

A stock solution of styrene (2 mL) and carboxymethyl dithiobenzoate (27) (24.8 mg) was prepared. Aliquots (1 mL) were transferred to two ampoules which were degassed, sealed and heated at 100 °C. The results are summarized in Table 26 below.

20

**Table 26: Molecular weight and conversion data for polystyrene prepared with carboxymethyl dithiobenzoate (27) at 100 °C**

25

Entry	time/hr	M <sub>n</sub>	M <sub>w</sub> /M <sub>n</sub>	% Conv.
1	6	3 900	1.49	11.4
2	64	7 400	1.34	42.5

conversion). GPC results obtained after methylation of the diblock, gave polymer of  $M_n$  4718 and  $M_w/M_n$  1.18. ph

The following two examples illustrate the synthesis of triblock copolymers from a bifunctional chain transfer agent. In the first step, a linear polymer with thiobenzoylthio groups at each end is prepared. The second step provides an ABA triblock.

#### Example 71

**Preparation of poly(styrene-*block*-methyl methacrylate-*block*-styrene) in the presence of 1,4-bis(2-thiobenzoylthioprop-2-yl)benzene (10)**

*Step 1: Preparation of low polydispersity poly(methyl methacrylate) with a dithioester group at each end*

A stock solution (I) of azobisisobutyronitrile (20.26 mg) and methyl methacrylate (15 mL) in benzene (5 mL) was prepared. An aliquot of stock solution (I) (2 mL) was transferred to an ampoule and was used as a control experiment. 1,4-Bis(2-thiobenzoylthioprop-2-yl)benzene (10) (93.64 mg) was added to the remaining stock solution (I) to form stock solution (II). Aliquots (4 mL) of the stock solution (II) were transferred into ampoules which were degassed, sealed and heated at 60°C for the times indicated. The results are summarized in Table 35 below.

**Table 35: Molecular weight and conversion data for poly(methyl methacrylate) prepared with 1,4-bis(2-thiobenzoylthioprop-2-yl)benzene (10) at 60°C**

Entry	time/hr	$M_n$	$M_w/M_n$	% Conv.
1	2	5 400	1.32	9.8
2	4	12 200	1.22	23.3
3	8	23 600	1.18	49.9
4	16	45 800	1.15	98.5

*Step 2: Preparation of poly(styrene-*block*-methyl methacrylate-*block*-styrene)*

The 8 hour poly(methyl methacrylate) sample (1.55 g,  $M_n$  23 600,  $M_w/M_n$  1.18) was dissolved in ethyl acetate and transferred to an ampoule. The solvent was removed under reduced pressure and azobisisobutyronitrile (3.1 mg) and styrene (10 mL) were added. The resulting solution was degassed, sealed and heated at 60°C for 20 hours. After removal of all the volatiles, the title block copolymer (orange pink colour foam) was isolated (3.91 g, 26% conversion),  $M_n$  59 300,  $M_w/M_n$  1.76 (trimodal).

✓  
The star poly(*n*-butyl acrylate) (0.5 g,  $M_n$  23248,  $M_w/M_n$  2.22) and styrene (2 mL) were transferred into an ampoule degassed, sealed and heated at 110°C for 16 hours. After removal of all the volatiles, the star block copolymer was obtained (1.3 g, 71.4% conversion) with  $M_n$  82 500 and  $M_w/M_n$  2.16. *ML*

5

The following example demonstrates the synthesis of a graft copolymer based on the use of a polymer chain with pendant dithioester groups.

#### Example 74

##### 10 **Preparation of graft copolymers in the presence of 3- & 4-vinylbenzyl dithiobenzoates (19)**

*Step 1: poly(methyl methacrylate-co-vinylbenzyl dithiobenzoate)* *L*

A solution of vinylbenzyl dithiobenzoate (19) (100 mg, mixture of meta and para isomers), azobisisobutyronitrile (15 mg), methyl methacrylate (10 mL) in 15 2-butanone (10 mL) was placed in an ampoule, degassed, sealed and heated at 60 °C for 6 hours to give poly(methyl methacrylate-co-vinylbenzyl dithiobenzoate) (3.52 g, 37.6 % conversion). GPC:  $M_n$  102 000,  $M_w/M_n$  2.26.

$^1\text{H}$ -nmr analysis indicates an average of 3.5 thiobenzoylthio groups per polymer chain.

20

*Step 2: Poly(methyl methacrylate-graft-styrene)*

A degassed solution of the poly(methyl methacrylate-co-vinylbenzyl dithiobenzoate) from step 1 (0.5 g) and azobisisobutyronitrile (1.0 mg) in freshly distilled styrene (5.0 mL) was heated at 60 °C for 40 hours. The polymerization 25 gave a red gel which was insoluble in THF, acetone and chloroform. The finding that polystyrene homopolymer could not be extracted from the mixture indicates the success of the grafting experiment.

#### Example 75

##### 30 **Preparation of low polydispersity poly(methyl methacrylate) by emulsion polymerization at 80°C in the presence of 2-phenylprop-2-yl dithiobenzoate (5)**

A 5-necked reaction vessel fitted with a condenser, thermocouple, and mechanical stirrer was charged with water (14.8 g), sodium dodecyl sulfate (3.0g 35 of 10% aqueous solution) and 2-phenylprop-2-yl dithiobenzoate (5) (0.325 g) and the mixture degassed under nitrogen at 90°C for 50 minutes. Feeds of methyl methacrylate (37.5 mL, 0.316mL/min) and 4,4'-azobis(4-cyanopentanoic acid) (900 mg) in water (85 g, 0.312mL/min) were then commenced. After 65 min the

concentration of the initiator feed was halved [4,4'-azobis(4-cyanopentanoic acid) (450 mg) in water (94 g, 0.312mL/min)]. On completion of the feeds, the reaction was held at 90°C for a further 90 minutes. The reaction mixture was sampled periodically to provide samples for GPC analysis (see Table 36 below).

5

**Table 36: Molecular weight and conversion data for poly(methyl methacrylate) prepared with 2-phenylprop-2-yl dithiobenzoate (5) at 90°C in emulsion**

Entry	MMA added (mL)	M <sub>n</sub>	M <sub>w</sub>	M <sub>w</sub> /M <sub>n</sub>	% Conv
1	20.5	3 550	4 530	1.27	14.2
2	37.5	12 000	15 800	1.32	41.4
3	final	26 000	34 900	1.33	89.8

- 10 The following three examples demonstrate the 'one-pot' synthesis of block copolymers by sequential monomer addition.

#### Example 76

- 15 **Preparation of poly(methyl methacrylate-*block*-styrene) by emulsion polymerization at 80°C in the presence of 2-phenylprop-2-yl dithiobenzoate (5)**

- A 5-necked reaction vessel fitted with a condenser, thermocouple, and mechanical stirrer was charged with water (37.5 g) and sodium dodecyl sulfate (3g of 10% aqueous solution). The mixture was degassed at 80°C under nitrogen for 20 40 minutes and a solution of 4,4'-azobis(4-cyanopentanoic acid) (71 mg) and 2-phenylprop-2-yl dithiobenzoate (5) (18.1 mg) in methyl methacrylate (1.6 g) was added as a single shot. Further 2-phenylprop-2-yl dithiobenzoate (5) (108 mg) in methyl methacrylate (2.5 g) was then added over 10 minutes. A feed of methyl methacrylate (15 g) was commenced at a rate of 0.188mL/min by syringe pump. 25 This was followed immediately by a feed of styrene (24 mL) at a rate of 0.2mL/min. Further initiator (31.5 mg) was added every 90 minutes during the feed periods. The reaction was held at 80°C for a further 120 minutes. The reaction mixture was sampled periodically to provide samples for GPC analysis (see Table 37 below).

completion of the feeds the reaction mixture was held at 80°C for a further 90 *hrs* minutes. The reaction mixture was sampled periodically for GPC analysis.

**Table 38: Molecular weight and conversion data for poly(butyl methacrylate) and poly(butyl methacrylate-*block*-styrene) prepared with phenylprop-2-yl dithiobenzoate (5) at 80°C in emulsion**

Entry	Sample	M <sub>n</sub>	M <sub>w</sub>	M <sub>w</sub> /M <sub>n</sub>	% Conv	M <sub>n</sub> (calc)
1	+10.9 mL BMA	26 000	39 000	1.50	54	22 585
2	+16.01 g BMA	63 000	77 000	1.22	95	57 742
3	final	65 500	81 000	1.23	>99	60 876
4	+11.4 mL Styrene	70 500	115 000	1.63	84	91 846
5	+15 g Styrene	78 000	136 000	1.74	84	98 579
6	Reaction Final	103 000	177 000	1.73	>99	105 710

#### Example 78

**Preparation of low polydispersity poly(styrene-*block*-methyl methacrylate) by emulsion polymerization in the presence of benzyl dithioacetate (12)**

- 10 Water (50 g) and sodium dodecyl sulfate (3g of 10% aqueous solution) were charged to a 5-neck reaction vessel equipped with a condenser, thermocouple, and mechanical stirrer. The mixture was heated at 80°C for 40 minutes while purging with nitrogen. A solution of 4,4'-azobis(4-cyanopentanoic acid) (87.5 mg) and benzyl dithioacetate (12) (104.2 mg) in styrene (2.3 g) was
- 15 then added as a single shot. Feeds of styrene (13.6 g, 0.2mL/min) and an initiator solution (4,4'-azobis(4-cyanopentanoic acid) (531mg, 0.089mL/min) in water (100 g)) were commenced. On completion of the feeds the reaction temperature was increased to 90°C and the addition of feeds of methyl methacrylate (15 mL, 0.316mL/min) and 4,4'-azobis(4-cyanopentanoic acid) (265 mg) in water (100 g)
- 20 (0.312mL/min) was commenced. After completion of the feeds the reaction was held at 90°C for a further 60 minutes. The reaction mixture was sampled periodically for GPC analysis.

Table 39: Molecular weight and conversion data for poly(styrene) and poly(methyl methacrylate-*block*-styrene) prepared with benzyl dithioacetate in emulsion *phc*

Entry	Sample	M <sub>n</sub>	M <sub>w</sub>	M <sub>w</sub> /M <sub>n</sub>	% Conv	M <sub>n</sub> (calc)
1	+6 mL styrene	7 690	10 500	1.37	43	4 560
2	+12mL styrene	22 000	29 000	1.33	89	1 824
3	+15 mL styrene	24 000	32 000	1.35	>99	25 480
4	+7.5 mL MMA	35 000	49 000	1.41	92	36 390
5	+15 mL MMA	39 000	61 000	1.56	84	45 513
6	Final	41 000	65 000	1.57	87	47 620

- 5 The following two examples demonstrate the synthesis of narrow polydispersity polymers by solution polymerization including a monomer feed.

#### Example 79

- 10 Preparation of low polydispersity poly(*n*-butyl acrylate) by the solution feed polymerization of butyl acrylate at 60°C in the presence of 1-phenylethyl dithiobenzoate (4)

- 15 *n*-Butyl acrylate (10 g), ethyl acetate (10 g), azobisisobutyronitrile (50 mg) and 1-phenylethyl dithiobenzoate (4) were placed in a 100mL 3-neck round bottom flask equipped with a condenser, mechanical stirrer and thermocouple, and degassed with nitrogen over 40 minutes with stirring. The flask was then placed in a pre-heated water bath at 60°C. After 60 minutes a solution of *n*-butyl acrylate (10 g) in ethyl acetate (5 g) was added over 3 hours (0.088 mL/min) by syringe pump. On completion of the feed the reaction was held at 60°C for a further 120 minutes. The reaction mixture was sampled periodically for GPC analysis.